

Valence-state imaging of mineral micro-intergrowths

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INTRODUCTION

The crystal chemistry and textural relationships of minerals hold a vast amount of information relating to the formation, history and stability of natural materials. An understanding of the detailed crystal chemistry of minerals within rocks, meteorites, soils, sediments, mineral-fluid/biota interfaces etc. will ultimately develop both an understanding of the processes involved with their formation and also a knowledge of their properties, reactivity and stability within their current environment. The acquisition of such knowledge is, however, non-trivial, due in no small part to the vast array of textural relationships and mineral assemblages observed, combined with their polygenetic history.

Minerals generally comprise complex structures with large unit cells that contain complex and varied crystal chemistries. For example, the 3d transition metals impart a significant influence on mineral properties and behaviour, existing at major, minor and trace concentrations and also exhibiting multiple valence states. Knowledge of the valence state ratios of these metals within minerals and mineral assemblages is fundamental to the calculation of geochemical variables such as pressure, temperature and oxygen fugacity. The application of soft X-ray spectroscopy to mineralogical material has revealed that 2p($L_{2,3}$) spectra provide a sensitive fingerprint of the electronic states of 3d metals [1-4]. In bulk powdered samples much of the textural and microstructural information is lost, but the area-selectivity capability of X-ray Photo-Emission Electron Microscopy (XPEEM) provides the ability to obtain valence state information from mineral intergrowths with a submicron spatial resolution [5,6,7].

RESULTS

Sulphide Intergrowths

Pentlandite, $(\text{Fe,Ni})_9\text{S}_8$, is the primary sulphide ore of Ni and usually occurs intergrown with the iron sulphide pyrrhotite, FeS. Figure 1 shows data obtained using the PEEM2 beamline at ALS and reveals the high quality of imaging and XAS data that can be obtained from XPEEM. The left hand image has an estimated field of view $< 20\mu\text{m}$ and was taken at 715.0eV, the main feature of the FeS pyrrhotite Fe $L_{2,3}$ spectrum. It thus shows the distribution of Fe in the chemical state equivalent to that of Fe in pyrrhotite. The light grey areas represent Fe from pyrrhotite, whereas the dark grey regions represent the Fe in pentlandite. The Fe $L_{2,3}$ spectrum below the image has been collected from the full image area. XPEEM allows an area selectivity such that an Fe $L_{2,3}$ spectrum can be obtained from any area of the image, thus providing a spatial resolution in the order of $0.1\mu\text{m}$. The right hand image, with an estimated field of view $< 40\mu\text{m}$, is taken at 864.5eV the main feature of the $(\text{Fe,Ni})_9\text{S}_8$ pentlandite Ni $L_{2,3}$ spectrum and the Ni $L_{2,3}$ spectrum from the whole image is below this image. Close investigation has shown banding of nickel and iron, with possible variations in the chemical state of the iron, in the ‘feathers’ of the pentlandite on a sub 200nm scale.

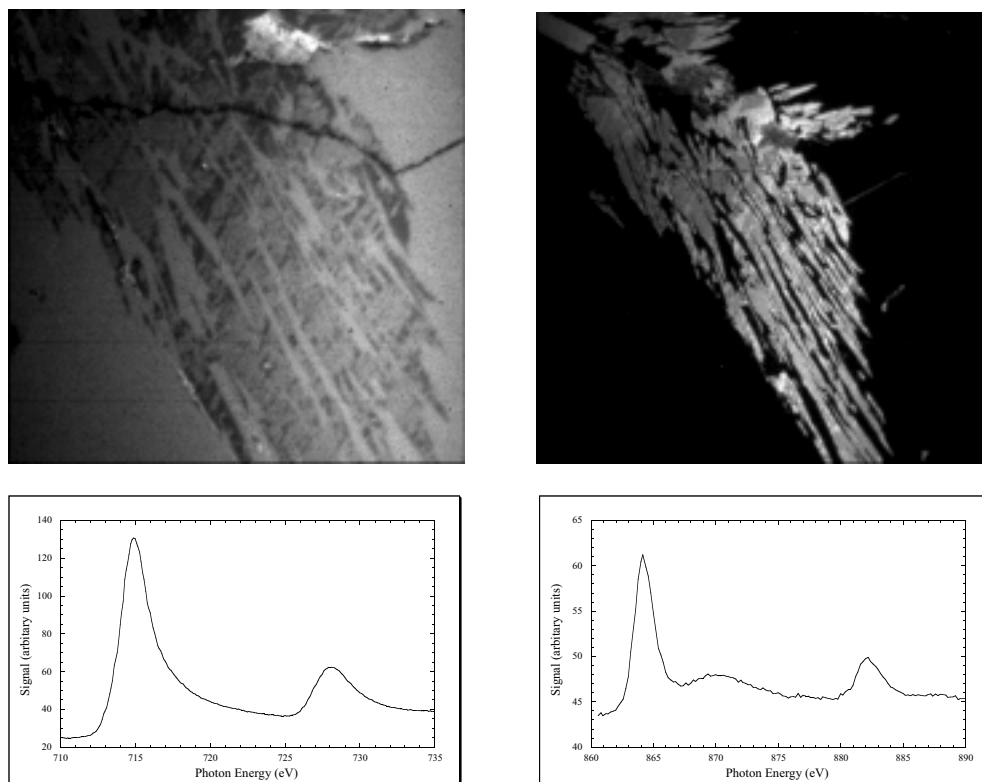


Figure 1. PEEM2 images from a pentlandite/pyrrhotite intergrowth. The left hand image is taken at 715.0eV – the main feature of the Fe L_{23} spectrum (below), and the right hand image was recorded at 864.5eV – the principal feature of the Ni L_{23} spectrum (below).

Hydrothermal Vent Sediments

Sulphide-to-oxide alteration behaviour in sea-floor hydrothermal vent samples recovered from the North Atlantic may potentially be observed from metal and sulphur valence information on a microscopic length scale. $\text{Mn}^{2+}/\text{Mn}^{3+}/\text{Mn}^{4+}$ ratios as well as $\text{Fe}^{3+}/\text{Fe}^{2+}$ are likely to be related to the extent of sulphate-reducing bacteria active at different horizons in these recent sea-floor hydrothermal deposits. Little is known about the micro-ecology in which these bacteria live, however it is thought that they are able to substantially modify their environment due to large differences observed in the redox conditions of various minerals contained in different strata of sea floor cores. Figure 2 shows iron, copper and oxygen chemical state images in a sample taken from the sediment around an active hydrothermal vent on the mid-Atlantic ridge. The unconsolidated sediment has been embedded in epoxy resin, sliced and polished but still provides excellent images and $L_{2,3}$ spectra.

The PEEM2 images show clear growth features that may reflect differing environments, oxidizing conditions and micro-ecologies. The top images show alternating Cu and Fe growth rings on the submicron scale indicating a low oxygen environment. The lower images show a submicron thick, copper sulphide precipitate that has grown around an iron sulphide grain. This ring represents both a different source fluid and a more reduced environment to that of the bulk Fe-oxides present in the image.

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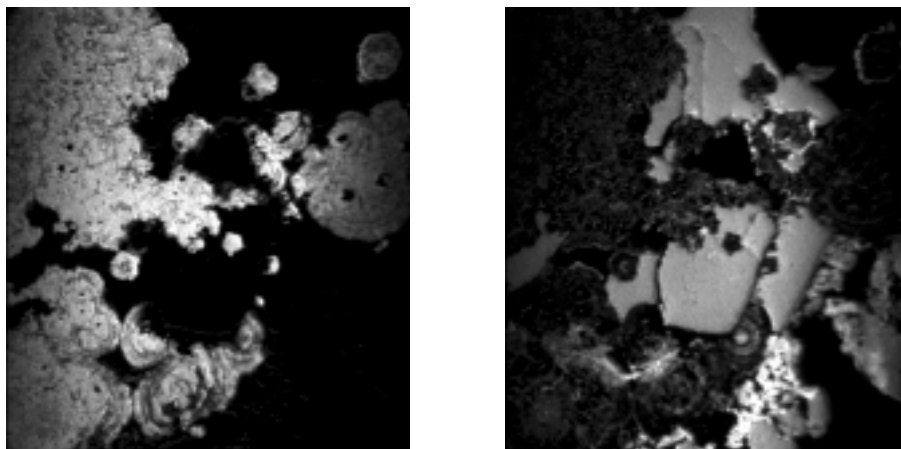


Figure 2. PEEM2 chemical state images from a sediment associated with a mid-Atlantic ridge hydrothermal vent. The top images are Cu (left) & Fe (right) and have a field of view of $<30\mu\text{m}$ and reveal clear botryoidal textures or growth features that may be related to bacterial micro-ecological cycles. The lower images are Fe (left), Cu (middle) & O (right) and have a field of view of $<20\mu\text{m}$. The Cu 'ring' appears to be a sulphide precipitate with a thickness of about $0.5 < 30\mu\text{m}$ that has grown around an Fe sulphide grain. The majority of the Fe phases in these images are clearly oxidized



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